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Cryogenic Oxidizers: Solid Oxygen and Ozone-Doped Solid Oxygen

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Introduction

One approach to the task of increasing the energy of a propellant system is to freeze gaseous oxygen into a solid grain and then trap energetic additives, such as ozone, in the grain. This technique would serve to create a denser, more compact fuel or oxidizer grain with more energy than current systems such as LOX/LH_2.

The first step in this process was illustrated with the Solid Oxygen (SOX) engine, which was the result of a Phase II SBIR with Orbital Technologies Corporation (ORBITEC). The objective of this SBIR, to develop an apparatus which would freeze and combust solid oxidizers with gaseous hydrogen, was demonstrated at ORBITEC with freezer and firing tests and was further carried out at the Phillips Laboratory.

The next step is to find a way to safely handle ozone and to demonstrate that ozone can be trapped in solid oxygen in significant concentrations. Unfortunately 100% ozone, especially in the liquid and solid phases, is notoriously dangerous because of its tendency to explode. However, numerous reports from the 1950's state that liquid oxygen/ozone mixtures can be produced and handled safely without incident. Additionally, the recent work of Chuck Wight has shown that solid ozone can be safely handled as an amorphous solid.[1] This information leads us to believe that solid mixtures of oxygen and ozone could be stable and safe enough to handle, thus providing a feasible additive to solid oxygen. Before ozone can be integrated into a solid oxygen grain, small scale experiments to explore its properties must be performed and evaluated. An apparatus has been designed and built to not only test sensitive ozone/oxygen mixtures, but any solid cryogenic propellant or oxidizer sample.

SOX Engine Demonstrations

The SOX engine was delivered to the Phillips Laboratory in April 1996. Prior to the engine's delivery, ORBITEC performed numerous freezer and firing tests in the engine as part of the contract requirements. After delivery, 6 runs were performed at the PL. The objective of these experiments was to demonstrate that the engine's chamber pressure could be controlled during combustion by varying the main hydrogen pressure. Oxygen grains as large as 275g have been frozen and combusted at chamber pressures as high as 200 psi.

Figure 1 shows a representative chamber pressure vs. time plot. It can be noted that the incoming hydrogen pressure does seem to have an effect on the resulting chamber pressure, although some fine-tuning still needs to be done to reliably control the chamber pressure.

Improved video techniques for the last 3 runs allowed us to observe a disturbing and reproducible occurrence. Within 1 - 2 seconds of the start of combustion, pieces of solid oxygen can be seen breaking off of the grain. Approximately half-way into the combustion, the grain is also observed to slip 1-2 cm down the tube. Preliminary analysis shows that the slipping can be correlated to a drop in the chamber pressure, though more analysis needs to be done before this can be stated with certainty. One possible solution for the slipping problem is to place a support ring at the bottom of the tube, directly under the grain, to prevent the grain from sliding. An approach to the sloughing problem may be to add a metal (such as Al) foam or matrix to the grain. This would have the added benefit of providing additional energy to the system.

Increasing the Energy of Solid Oxygen

Following the successful demonstration of solid oxygen combustion, we turned our attention to increasing the energy of this oxidizer--a goal of the HEDM program. Ozone has long been considered as an energetic additive to liquid oxygen and more recently as an additive to solid oxygen. Calculations show that 50 mole % ozone in oxygen will increase the I_{sp} to 410 sec, a 20 sec increase over that of pure solid oxygen.[2] This energy benefit, along with ozone being relatively easy to produce and measure, makes ozone our primary additive candidate.

Gaseous and liquid ozone are well-characterized, and methods exist to handle it safely at any concentration. Much work was done on liquid ozone and liquid oxygen mixtures in the 1950's, when these liquid mixtures were considered for high energy liquid rocket oxidizers. A considerable amount of data on liquid ozone and liquid ozone/oxygen mixtures exists and explains that these mixtures can be produced and handled safely:

- "The minimum concentration of liquid ozone in oxygen which can be made to explode by passage of an electric spark through the body of the liquid has been determined to be 47 percent ozone by weight."[3]
- "Detonation data indicate that 30 percent by weight ozone in liquid oxygen if properly handled can be run safely in a rocket."[4]
- "The investigations of Mahieux [in a French patent] indicated that in the temperature range between 123 and 93 K, liquid ozone-oxygen mixtures are stable up to an ozone concentration of 60 mole percent with no tendency to explosion on the application of any kind of shock effect."[5]
- "It has been the experience of the staff of Armour Research Foundation that highly concentrated ozone, as either a gas or a liquid, can be produced and handled in pilot plant quantities with care and without mishap."[6]
- "100% liquid ozone and all liquid ozone/oxygen mixtures, if properly prepared and very carefully handled, are relatively stable."[6]

Considerably less literature exists on solid ozone; no literature could be found dealing with solid ozone/oxygen mixtures. Ozone, notoriously dangerous because of its tendency to detonate when not handled carefully, is sometimes said to be even more hazardous in the solid state.

> "It is, therefore, recommended that ozone should not be stored or transported as a solid and that its presence should be avoided at all times."[7]

"Solid ozone with solid carbon dioxide, nitrous oxide, and argon present has the same impact sensitivity as solid ozone alone. The use of solid ozone is to be avoided."[8]

On the other hand, a conflicting report states that "solid ozone (at -320° F) was compressed to 22.5 atm without any difficulty. Slight impact and slight friction at that temperature did not cause an explosion."[9]

More recent research into the properties of solid ozone has been conducted by Chuck Wight at the University of Utah and shows that solid ozone can be desensitized. Thick films (1 mm or greater) of the crystalline structure are highly unstable, detonating explosively under slight provocation. Yet amorphous samples of solid ozone formed at temperatures below 20K are stable to laser irradiation. (Because temperatures at which solid ozone was formed were not reported in the references above, this may explain the discrepancies.) Thin films of amorphous, polycrystalline, or crystalline structure are all stable, giving an indication of the critical diameter of solid ozone.[1]

Proposed Sensitivity Testing

Because of the dearth of literature on solid O_3/O_2 mixtures and the inconsistency of solid O_3 reports, we determined it necessary in the interest of safety to establish the limits of ozone's stability. An apparatus has been designed and built in which we will perform various sensitivity tests. Although these tests were designed with ozone/oxygen mixtures in mind, any cryogenic solid sample could be tested in the chamber. Ozone samples will be small, on the order of 10 - 100 mg. Initial ozone concentrations will be low and then gradually increased, to build a comprehensive data base of sensitivity information. The entire operation will be remotely controlled.

Initial tests will be cryogenic adaptations of conventional propellant tests such as drop or impact tests, hot-wire, and friction tests which have not been previously performed at temperatures near absolute zero. Standards will be tested along with the ozone/oxygen samples to use as a basis of comparison.

If the tests show that solid ozone/oxygen mixtures are safe enough to handle, the mixtures will be scaled up to a size suitable for combustion in the SOX engine. If not, this research will at least answer fundamental questions which are currently not addressed in literature.

Summary/Conclusions

- The Solid Oxygen Engine is a valuable tool for testing cryogenic HEDM propellant systems. Engine firings have demonstrated that pure, undoped solid oxygen/gaseous hydrogen can be combusted in the engine and that the chamber pressure can be controlled during combustion by varying the H_2 pressure.

- Theory predicts that adding 50% ozone to solid oxygen will increase the I_{sp} by 20 sec. We will determine experimentally if ozone is a feasible additive to solid oxygen.

- Based on the literature on liquid and gaseous ozone, extreme caution will be used when testing ozone/oxygen mixtures. An apparatus has been designed and built and conventional propellant tests

have been adapted for our cryogenic environment. Specific milestones will have to be passed before proceeding to each new step in the testing sequence.

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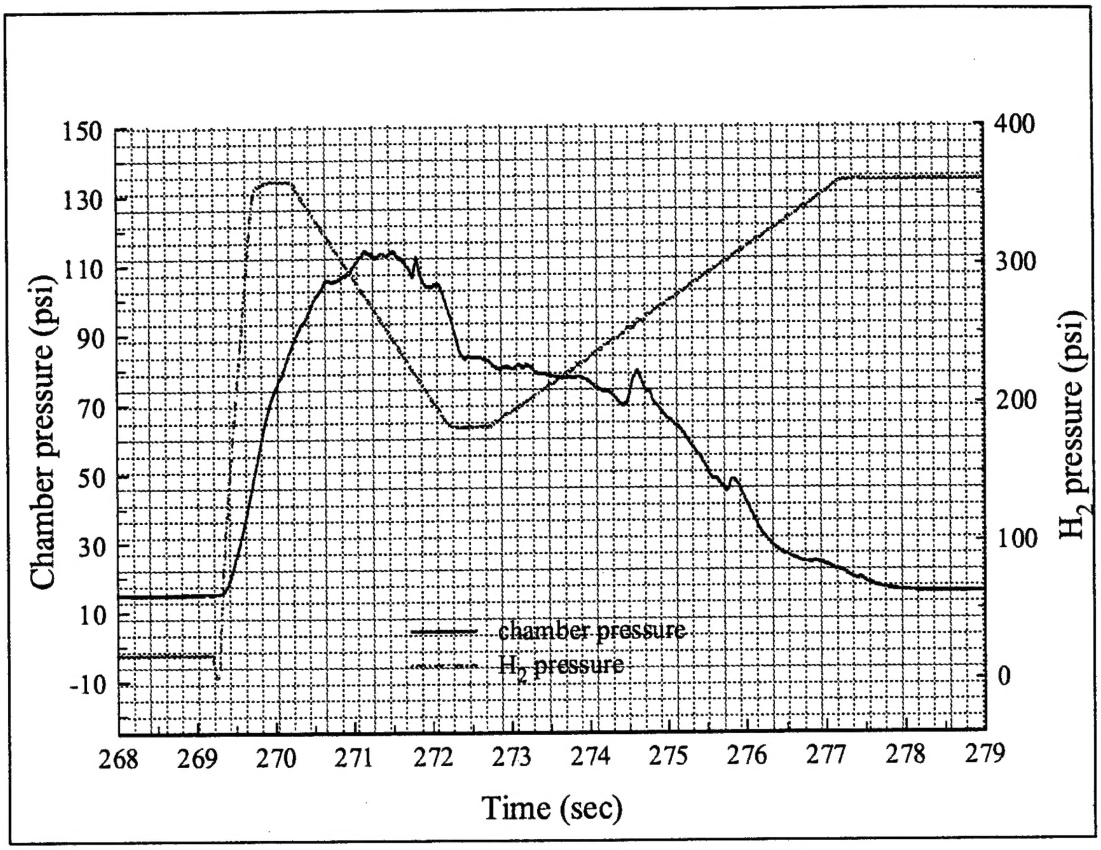

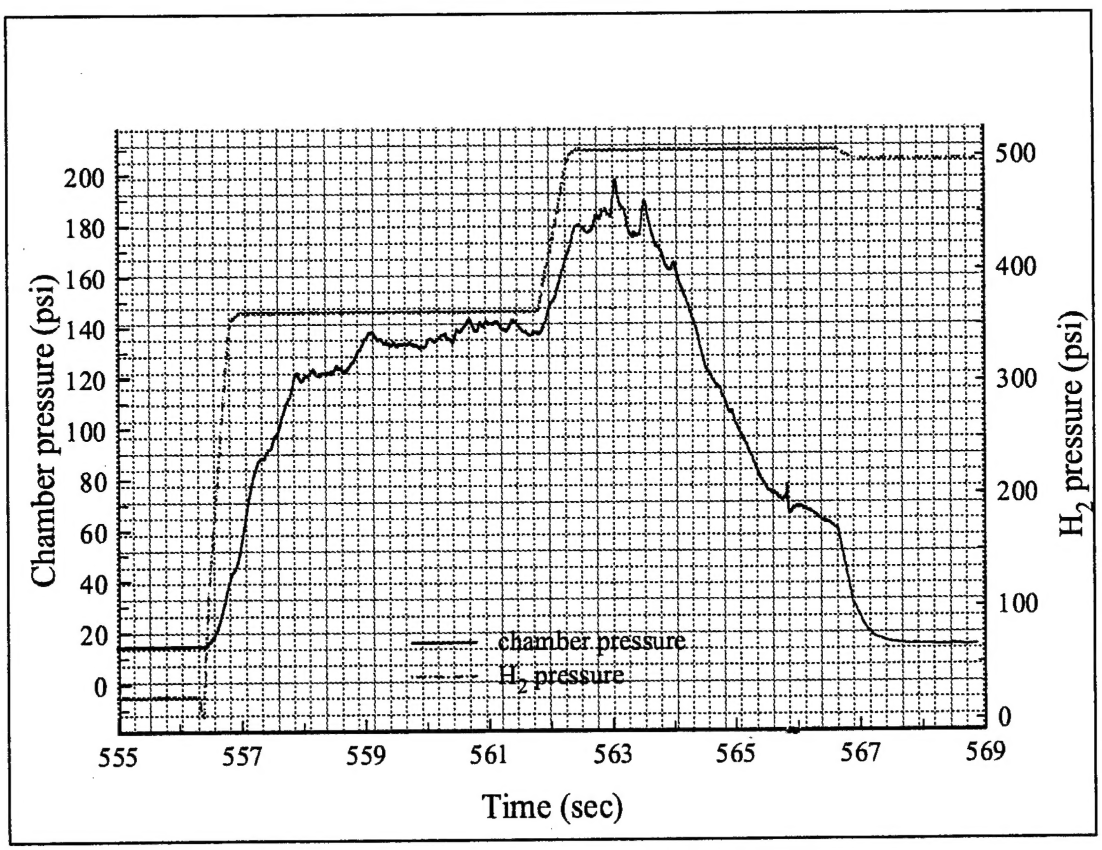

Figure 1. a.) Chamber pressure vs. time with corresponding hydrogen pressure for a 150g solid O_2 grain. b.) Similar plot, but for a 275g solid O_2 grain.